Supplementary Material (ESI) for Green Chemistry

Electronic Supplementary Information

Title: An efficient and heterogeneous recyclable palladium catalyst for chemoselective conjugate reduction of α,β-unsaturated carbonyls in aqueous medium

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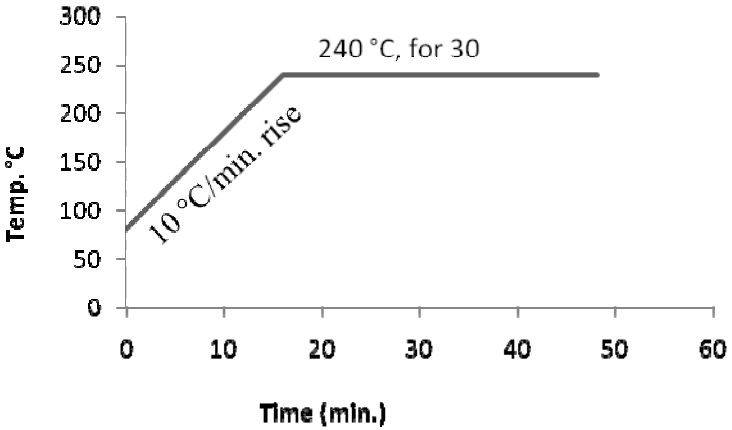
A) Typical experimental procedure for chemoselective conjugates reduction of benzylideneacetophenone

In a 10 mL deionised water, 1 mmol of benzylideneacetophenone, 3 mmol of HCOONa and polymer supported Pd-NHC catalyst (50 mg, 0.015 mmol) were added in round bottom flask and the reaction mixture was stirred at 100 °C for 12 h. The progress of the reaction was monitored using GC analysis (Perkin Elmer, Clarus 400) (BP-10 GC column, 30 m × 0.32 mm ID, film thickness 0.25 mm). On completion, the reaction mixture was cooled to room temperature and the products were extracted with ethyl acetate, dried over Na_2SO_4 and the solvent was evaporated under vacuum. The obtained crude product was then purified by column chromatography using silica gel, (100–200 mesh size,) with petroleum ether/ethyl acetate (PE–EtOAc, 95:05) as eluent to afford pure product.

Temperature programme for GC-MS Analysis



All products are known, which were confirmed by GC-MS analysis. Some of the selected compounds were characterized by different spectroscopic techniques such as ^{1}H NMR (Varian Mercury, 400 MHz NMR Spectrometer), ^{13}C NMR spectra (75.43 MHz), GC-MS (Shimadzu GC-MS QP 2010) (Rtx-17, 30 m × 25mmID, film thickness 0.25 µm df) (column flow- 2 mL/min, 80 °C to 240 °C at 10°/min. rise.) and IR (Perkin-Elmer FT-IR) spectroscopic techniques.

B) A typical procedure for the preparation of polymer supported palladium-*N*-heterocyclic carbene (PS-Pd-NHC) catalyst

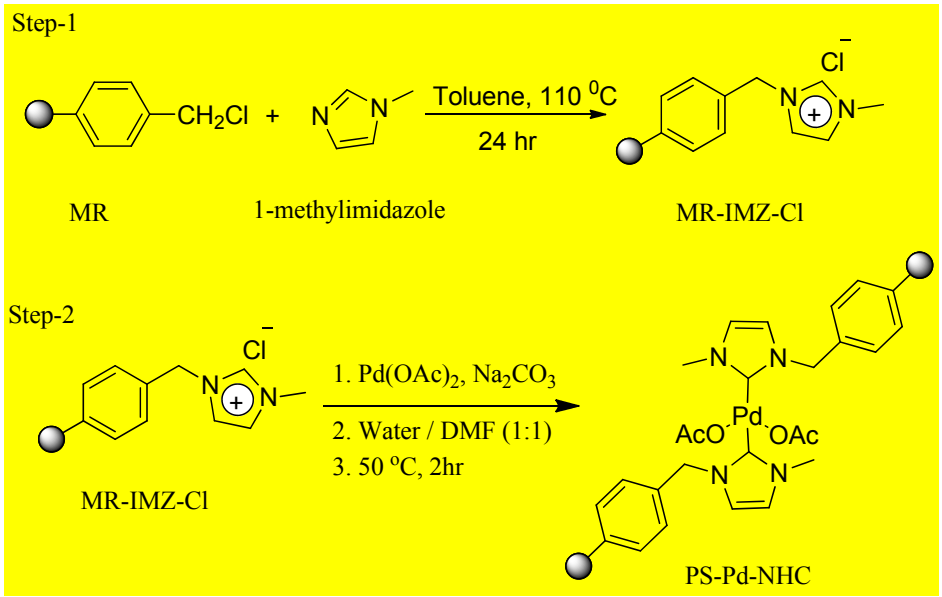
Step-1 Preparation of imidazolium-loaded polymeric support (MR-IMZ-Cl)

In 100 mL round bottom flask were added Merrifield peptide resin (2 % cross linked, 2.3 mmol Cl/g, Aldrich) 5 g, N-methyl imidazole (20 mmol) in toluene (50 mL) and refluxed for 24 hour. On completion, the reaction mixture was cooled to room temperature. It was then filtered and the residue obtained was washed with toluene, 0.1 mol/L HCl, water and methanol sequentially followed by drying under reduced pressure to afford imidazolium-loaded polymeric support MR-IMZ-Cl (loading of ionic liquid : 1.67 mmol/g, determined by elemental analysis). The catalyst was further characterized by FTIR to check the attachment of the ionic liquid. A strong band centred at 1569 cm^{-1} confirms the attachment of the imidazole on Merrifield resin.

Step-2 Preparation of polymer supported palladium-*N*- heterocyclic carbene complex with the imidazolium-loaded polymeric support (PS-Pd-NHC)

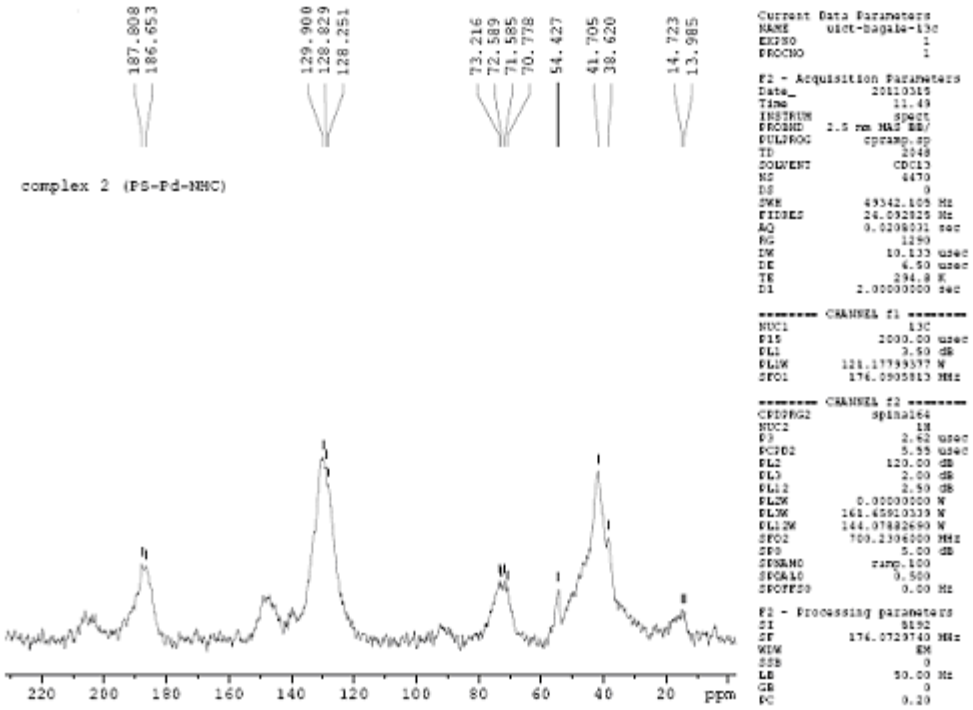
A mixture of the imidazolium loaded polymeric support (MR-IMZ-Cl) (1.0 g, 19.1 mmol/g) and $Pd(OAc)_2$ (0.225 g, 1 mmol) was suspended in DMF (20 mL). To this suspension an aqueous solution (20 mL) of Na_2CO_3 (1.06 g, 10.0 mmol) was added. The mixture was then sonicated at room temperature for 30 min and agitated in an orbital shaker at 50 °C for 2 h at 150 rpm. On completion, the reaction mixture was filtered and the polymeric support was washed vigorously with distilled water (10 mL × 5), MeOH (10mL × 5), and dried under reduced pressure to give PS-Pd-NHC. Prepared PS-Pd-NHC was then characterized by solid state ^{13}C NMR (Bruker Avance^{III} 700 MHz); δ 14 (CH_3 aliphatic acetate skeleton), 38 (N-CH_3 skeleton), 41 (aliphatic polystyrene skeleton), 128 (NCH, NCH, aromatic polystyrene skeleton), 147 (NCN, aromatic polystyrene skeleton), 187 (C=O acetate skeleton).

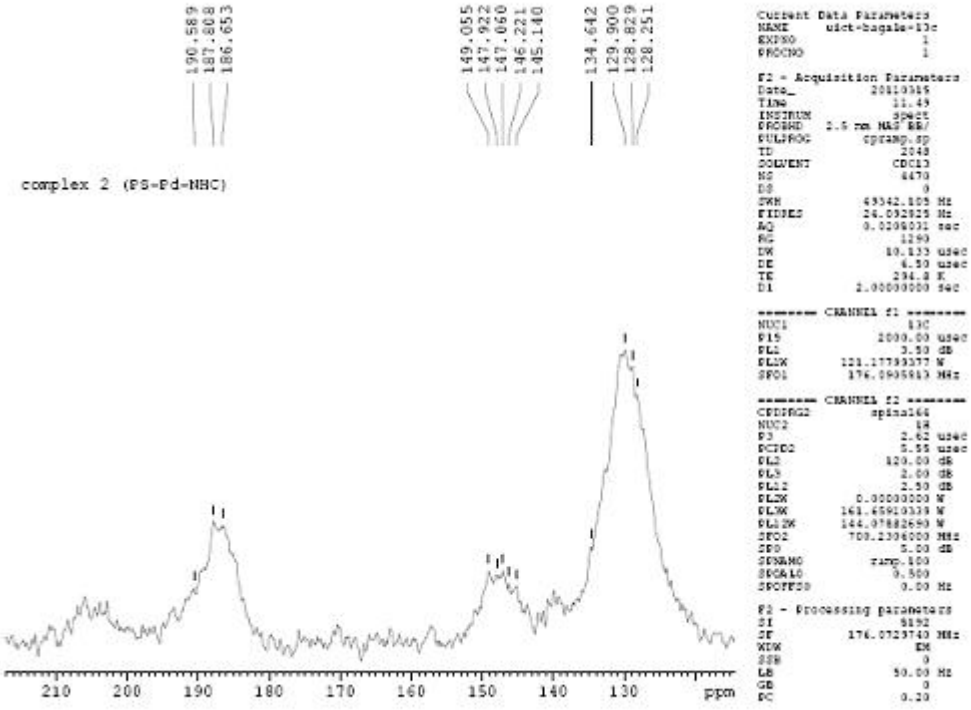
Schematic representation of preparation of PS-Pd-NHC catalyst



The amount of Pd loaded on the polymeric support was determined by using ICP-AES analysis. The polymer supported palladium-*N*- heterocyclic carbene complex (50 mg) was treated with a mixture (25 mL) of hydrochloric acid and nitric acid (1:1, v/v) at room temperature for 30 minutes. The orange-coloured solution formed was filtered, washed with distilled water. The filtrate and washing solution were combined to determine the amount of Pd by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and was found to be about 0.29 mmol/g of support.

Solid state ^{13}C NMR spectra of PS-Pd-NHC complex

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187.808
186.653
149.055
147.922
147.060
146.221
145.140
134.642
129.900
128.829
128.251
complex 2 (PS-Pd-NHC)
210
200
190
180
170
160
150
140
130
ppm
Current Data Parameters
NAME ulct-bugale-13c
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110315
TIME 11.49
INSTRUM spect
PROBHD 5 mm MAS BB/
PULPROG zgpg.sp
TD 2048
SOLVENT CDCl3
NS 6470
DS 0
SWH 49342.105 Hz
FIDRES 24.092825 Hz
AQ 0.0206031 sec
RG 1290
DW 10.133 usec
DE 6.50 usec
TE 294.8 K
D1 2.00000000 sec
======== CHANNEL f1 ========
NUC1 13C
P15 2000.00 usec
PL1 3.50 dB
PL1W 121.17793377 W
SFO1 176.0935813 MHz
======== CHANNEL f2 ========
CPDPRG2 spinal64
NUC2 1H
P3 2.62 usec
PCPD2 5.55 usec
PL2 120.00 dB
PL3 2.00 dB
PL12 2.50 dB
PL2W 0.00000000 W
PL3W 161.65919339 W
PL12W 144.97882690 W
SFO2 700.2306000 MHz
SPO 5.00 dB
SPNAM0 ramp.100
SPOAL0 0.500
SPOFF0 0.00 Hz
F2 - Processing parameters
SI 8192
SF 176.0723740 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 0.20

C) Characterisation data of some selected compounds:

1) 1, 3-Diphenyl-propan-1-one (Table 3 entry 1) White solid

^{1}H NMR (400 MHz, DMSO-d^{6}) δ=7.99(d, 2H, J=7.6 Hz), 7.6 (t, 1H, J=7.6 Hz), 7.5(m, 2H, J=8), 7.28 (d, 4H, J=7.6 Hz), 7.17 (d, 1H, J=7.2 Hz), 3.37 (t, 2H, J= 8), 2.94 (t, 2H, J= 7.6 Hz); ^{13}C (75 MHz, DMSO-d^{6}) 199.1, 141.2, 136.5, 133.1, 128.6, 128.3, 127.9, 125.8, 39.5, 29.4; IR (KBr) νmax/cm^{-1} 3061, 2927, 2341, 1957, 1824, 1681, 1595, 1494, 1448, 1208, 1075, 973, 928, 743, 701; GC-MS (EI) m/z (%) = 210(38) [M]$^{+}$, 106(9), 105(100), 91(12), 77(42), 51(11) Retention time- 14.8 minute.

2) 3-(4-Methoxy-phenyl)-1-phenyl-propan-1-one (Table 3 entry 2) White Solid

^{1}H NMR (400 MHz, DMSO-d^{6}) δ=7.97(d, 2H, J=7.2 Hz), 7.62 (t, 1 H, J=7.6 Hz), 7.51(t, 2H, J=8 Hz), 7.18(d, 2H, J=8.4 Hz), 6.83 (d, 2H, J=8.4 Hz), 3.7 (s, 3H), 3.32 (t, 2H, J=7.6), 2.8 (t, 2H, J=7.2); ^{13}C (75 MHz, DMSO-d^{6}) 199.2, 157.5, 136.6, 133, 129.4, 129.3, 128.6, 127.9, 113, 54.9, 39.2, 28.6; IR (KBr) νmax/cm^{-1} 3000, 2958, 2823, 2356, 1896, 1681, 1608, 1510, 1447, 1237, 1033, 825, 744; GC-MS (EI) m/z (%) =240(40) [M]$^{+}$, , 135(12), 122(9), 121(100), 108(18), 105(47), 77(41), 78(8), 51(8) Retention time- 18.1 min.

3) 4-Phenyl-butan-2-one (Table 3 entry 5) Colourless Oil.

1H NMR (400 MHz, DMSO-d6) δ=7.26 (t, 2H, J=7.6 Hz), 7.19 (d, 2H, J=8.4 Hz), 7.16(d, 1H, J=7.6 Hz), 2.76 (s, 4H), 2.1 (s, 3H); ^{13}C (75 MHz, DMSO-d^{6}) 207.5, 141.1, 128.9, 128.2, 125.7, 44.1, 29.6, 29.05; IR (neat) νmax/cm^{-1} 3027, 2928,

1716, 1603, 1496, 1453, 1358, 1161, 1030, 749, 699; GC-MS (EI) m/z (%) = 148(83) $[M]^+$, 147(4.5), 133(17), 106(10), 105(100), 104(14), 103(15), 91(74), 79(19), 78(16), 77(25), 65(14), 43(93) Retention time- 7.1 min.

4) Cyclohexanone (Table 3 entry 6) Colourless liquid

1H NMR (400 MHz, DMSO-d6) δ=2.25 (t, 4H, J=6.4 Hz), 1.76 (t, 4H, J=6 Hz), 1.65 (d, 2H, J=4.4 Hz); ^{13}C (75 MHz, DMSO-d^6) 210, 41.31, 26.5, 24.3; IR (neat) νmax/cm^{-1} 2938, 2863, 1711, 1449, 1421, 1338, 1311, 1222, 1119, 1052, 1018, 908, 864, 750; GC-MS (EI) m/z (%) = 98(39) $[M]^+$, 83(10), 70(24), 69(32), 55(100), 54(8), 43(12), 42(7), 41(34) Retention time- 2.8 min.

5) 3-(4-Chloro-phenyl)-1-phenyl-propan-1-one (Table 3 entry 8) off White solid.

^1H NMR (400 MHz, DMSO-d^6) δ=7.97(d, 2H, J=8 Hz), 7.62 (t, 1 H, J=7.2 Hz), 7.51(t, 2H, J=7.6 Hz), 7.33(d, 2H, J=8.8 Hz), 7.27 (d, 2H, J=8.8 Hz), 3.37 (t, 2H, J=7.6), 2.9 (t, 2H, J=7.6); ^{13}C (75 MHz, DMSO-d^6) 198.9, 140.3, 136.5, 133.1, 130.4, 130.3, 128.6, 127.9, 39.9, 28.7; IR (KBr) νmax/cm^{-1} 2929, 1967, 1903, 1682, 1492, 1448, 1261, 1094, 823,689; GC-MS (EI) m/z (%) =244(22) $[M]^+$, 106(8), 105(100), 77(43), 51(10) Retention time- 17.1 min.

6) 1-Phenyl-3-thiophen-2-yl-propan-1-one (Table 3 entry 10) White Solid.

^1H NMR (400 MHz, DMSO-d^6) δ=8.04(d, 2H, J=7.6 Hz), 7.69 (t, 1 H, J=7.2 Hz), 7.57(t, 2H, J=7.6 Hz), 7.34(d, 1H, J=4.4 Hz), 6.97 (d, 2H, J=4.4 Hz), 3.47 (s, 2H, J= 7.2), 3.2 (t, 2H, J=7.2); ^{13}C (75 MHz, DMSO-d^6) 198.5, 143.6, 136.4, 133.1, 128.6, 127.8, 126.7, 124.7, 123.6, 39.6, 23.5; IR (KBr) νmax/cm^{-1} 3104, 2923, 1980, 1683, 1595, 1446, 1363, 1207, 972,

747, 705; GC-MS (EI) m/z (%) =216(51) $[M]^+$, 111(56), 110(14), 105(100), 97(64), 84(10), 77(75), 51(21), 45(13) Retention time- 15.1 min.

7) 3-Furan-2-yl-1-phenyl-propan-1-one (Table 3 entry 11) Yellow Oil.

^{1}H NMR (400 MHz, DMSO-d^6) δ=8.0(d, 2H, J=8 Hz), 7.64 (t, 1 H, J=7.6 Hz), 7.53(d, 2H, J=7.6 Hz), 7.5(d, 1H, J=7.6 Hz), 6.34 (bs, 1H, J=8 Hz), 6.13 (bs, 1H, J=2.8 Hz), 3.38 (t, 2H, J= 7.2), 2.96 (t, 2H, J=7.2); ^{13}C (75 MHz, DMSO-d^6) 198.5, 154.6, 141.2, 136.44, 133.19, 128.7, 127.9, 105, 36.1, 21.9; IR (neat) νmax/cm^{-1} 3061, 2920, 1685, 1597, 1507, 1448, 1363, 1206, 1076, 1012, 975, 921, 803, 733, 689; GC-MS (EI) m/z (%) =200(45) $[M]^+$, 144(6), 106(9), 105(100), 95(35), 94(11), 91(14), 77(65), 53(12), 51(20) Retention time- 12.6 min.

Table 3 entry 1, ^{1}H

1,3-Diphenyl-propan-1-one

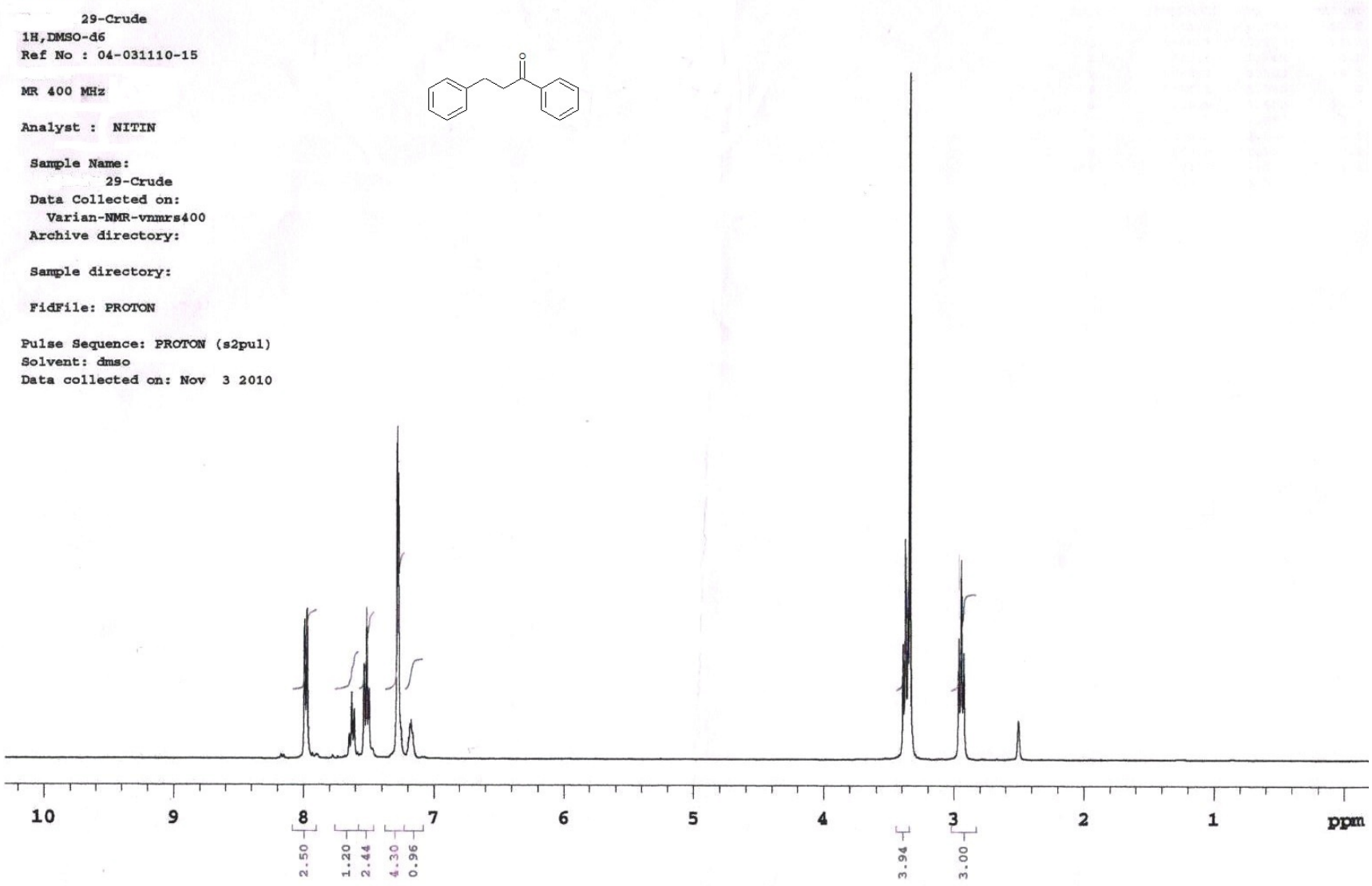

Table 3 entry 1, ^{13}C

1,3-diphenylpropan-1-one

R.NO-029

exp1 s2pul

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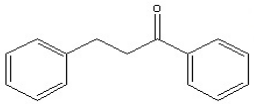

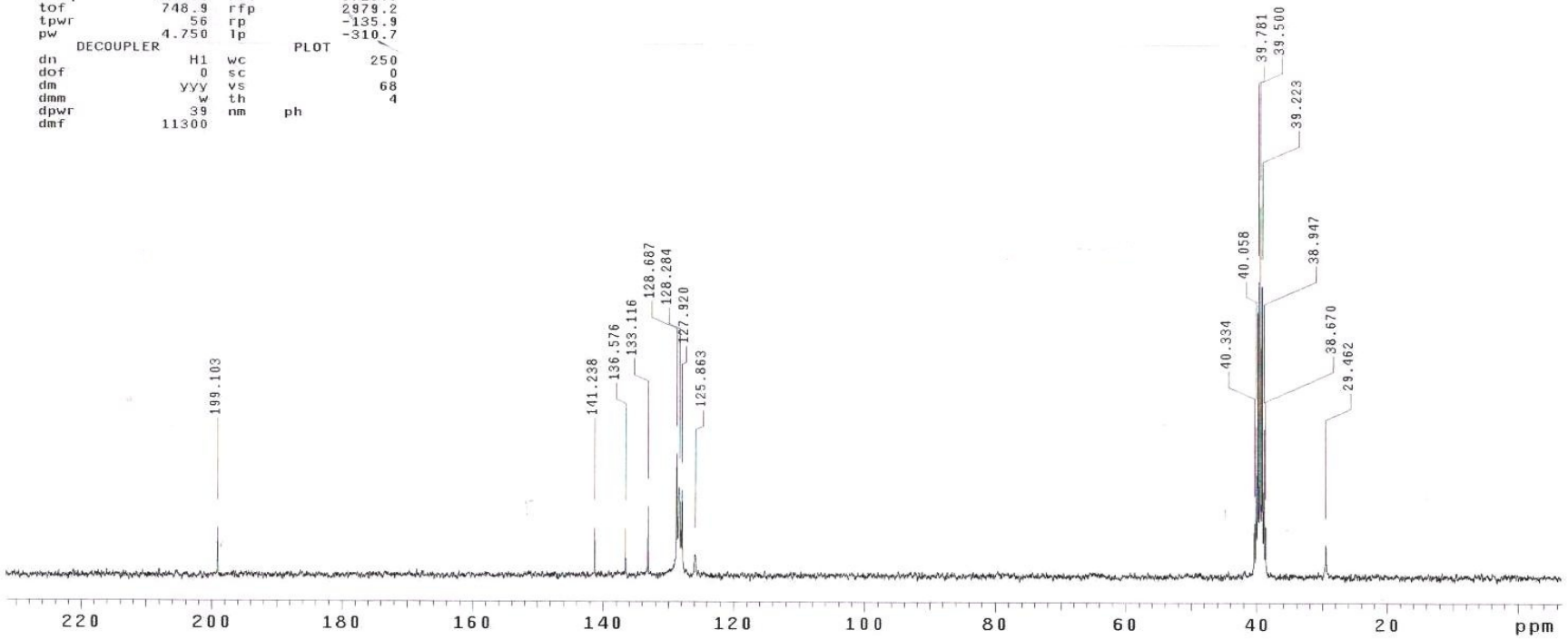

Table 3 entry 2, ^{1}H

3-(4-Methoxy-phenyl)-1-phenyl-propan-1-one

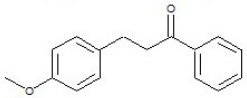

Table 3 entry 2, ^{13}C

3-(4-methoxyphenyl)-1-phenylpropan-1-one

R.No.041

exp1 s2pul

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np	87052	dp	y
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bs	4	PROCESSING	
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tof	748.9	rfp	2979.2
tpwr	56	rp	-120.7
pw	4.750	lp	-347.9
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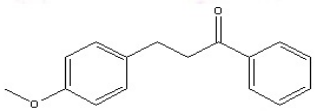

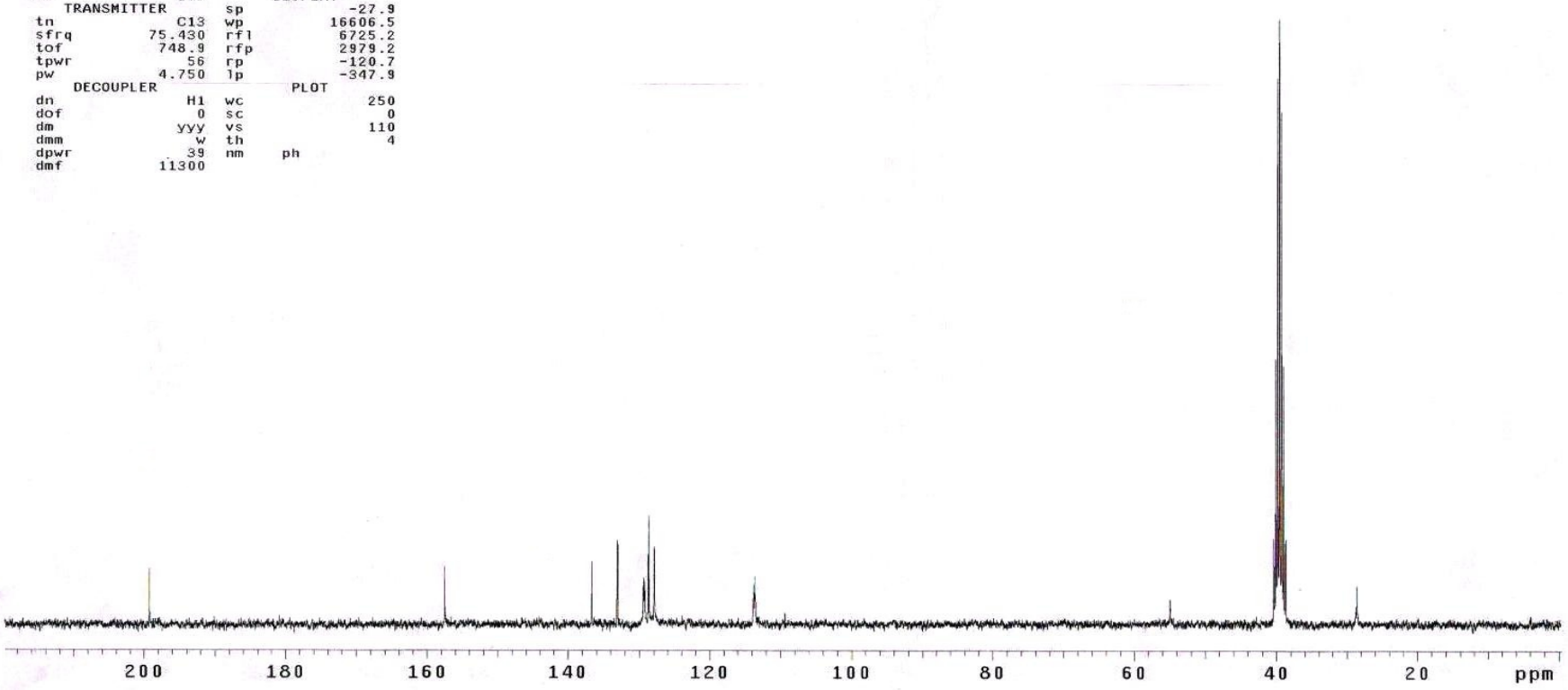

Table 3 entry 5, ^{1}H

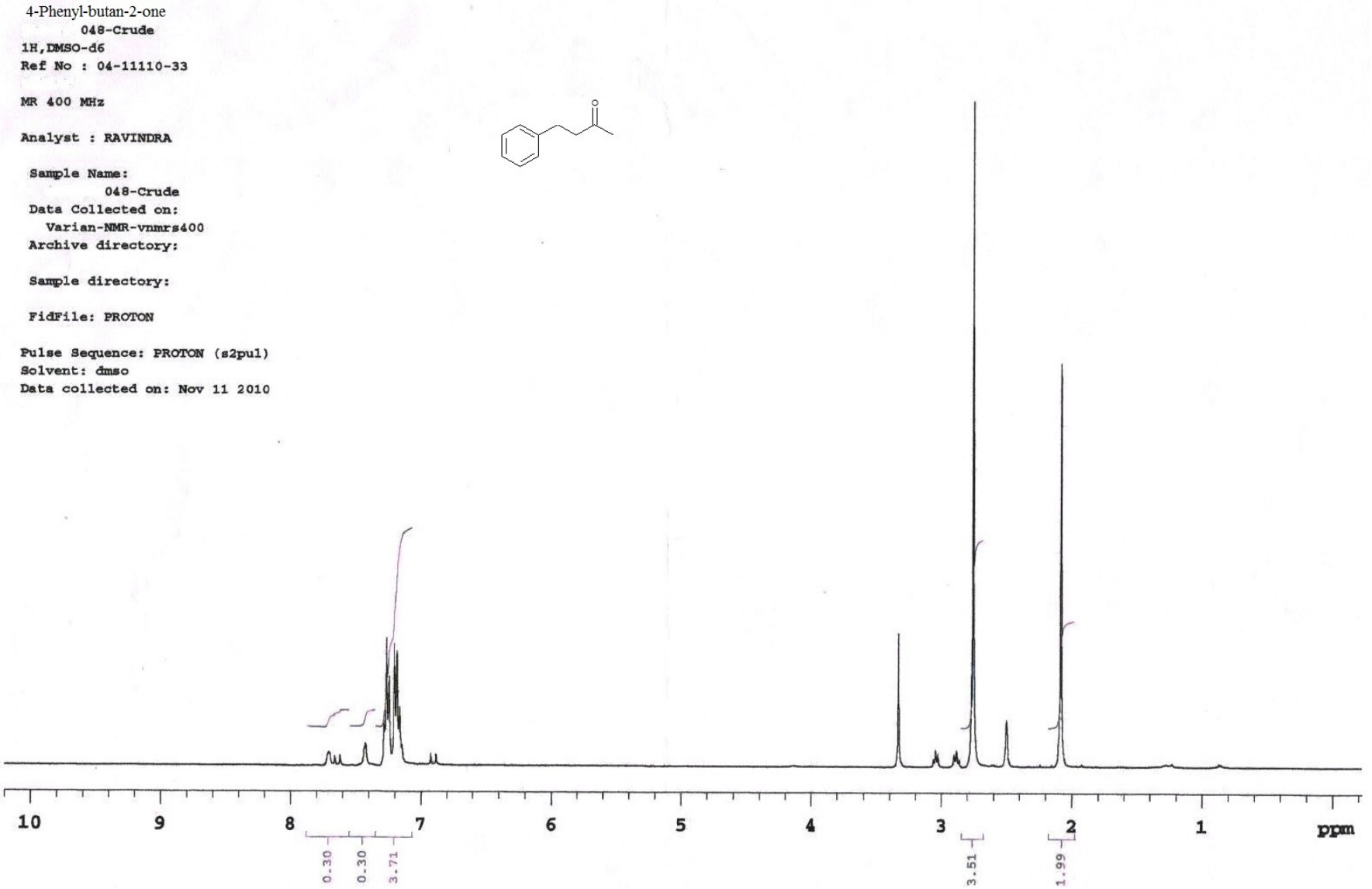

Table 3 entry 5, ^{13}C

4-phenylbutan-2-one

R.No-048

exp1 s2pul

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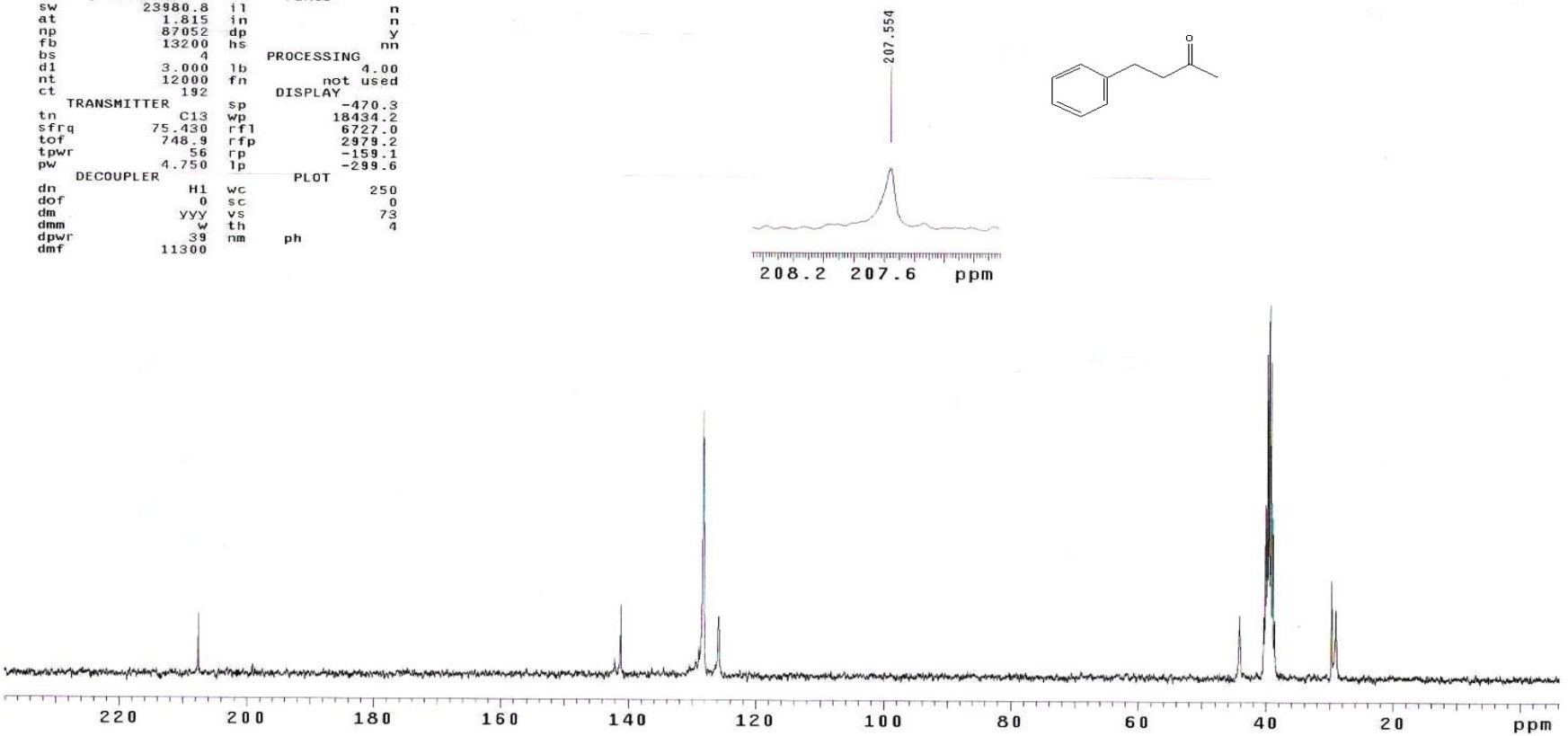

Table 3 entry 6, ^{1}H

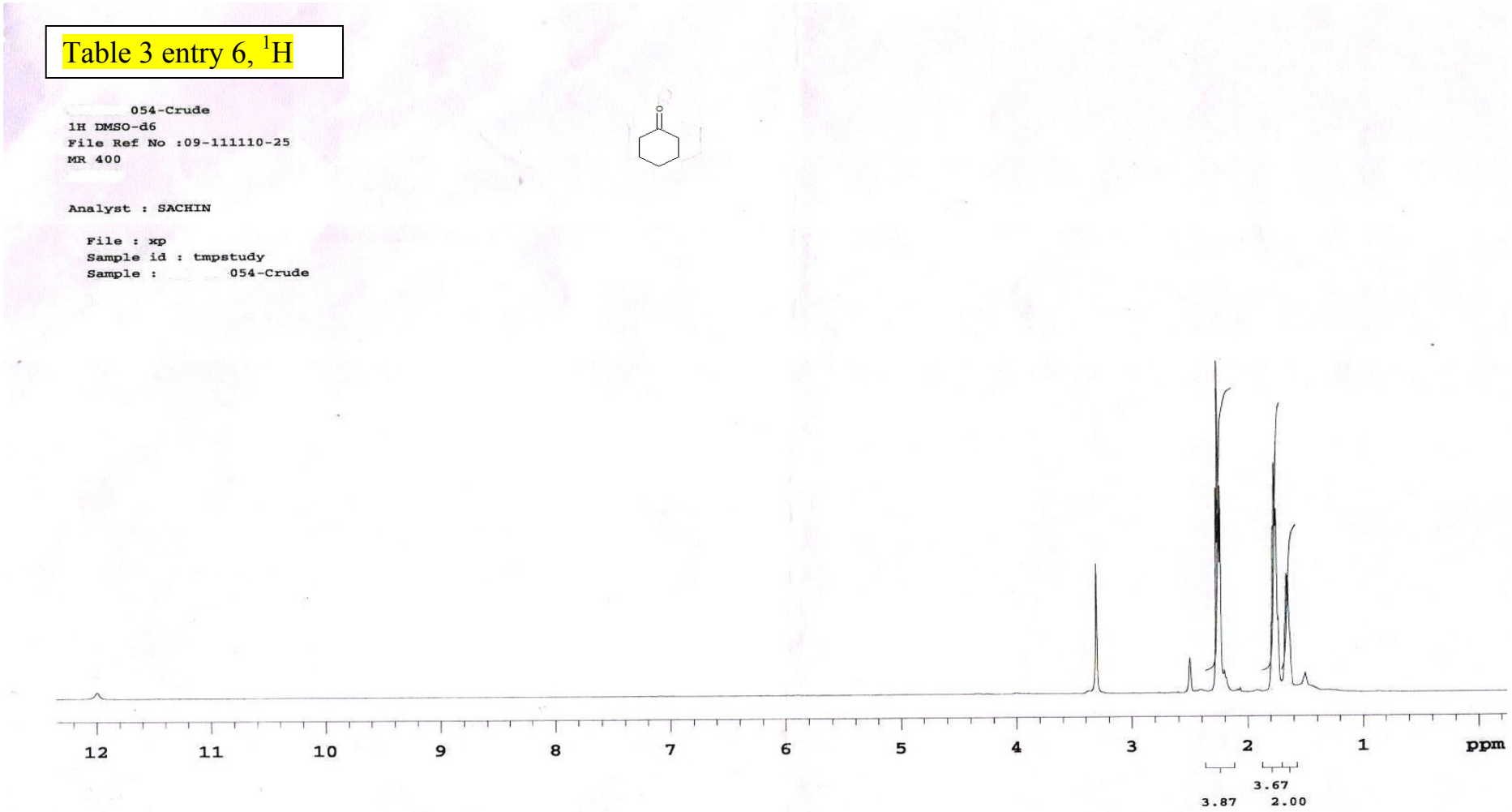

Table 3 entry 6, ^{13}C

cyclohexanone

Reaction No-054

exp1 s2pul

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XTERNAL/Dinsh-UICT~		pw90	11.500
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fb	13200	hs	nn
bs	4	**PROCESSING**	
d1	3.000	lb	4.00
nt	12000	fn	not used
ct	148	**DISPLAY**	
TRANSMITTER		sp	-494.1
tn	C13	wp	18371.3
sfrq	75.430	rfl	6719.4
tof	748.9	rfp	2979.2
tpwr	56	rp	-139.5
pw	4.750	lp	-303.1
DECOUPLER		**PLOT**	
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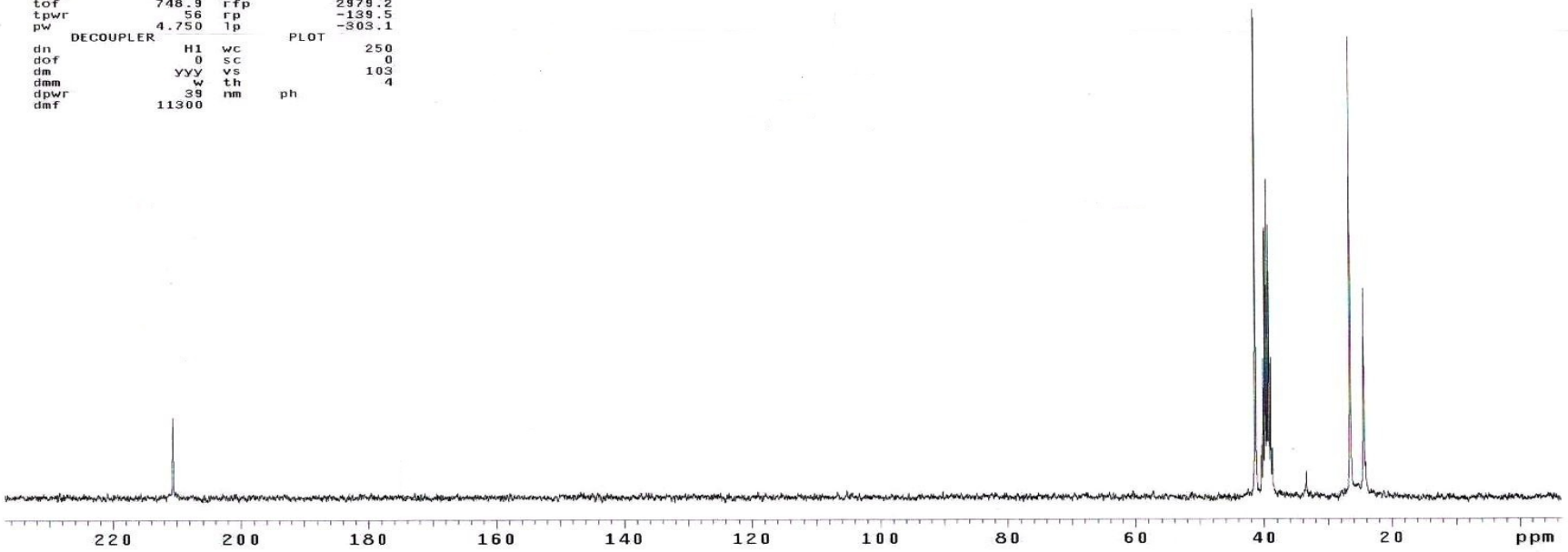
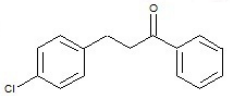


Table 3 entry 8, ^{1}H

3-(4-Chloro-phenyl)-1-phenyl-propan-1-one



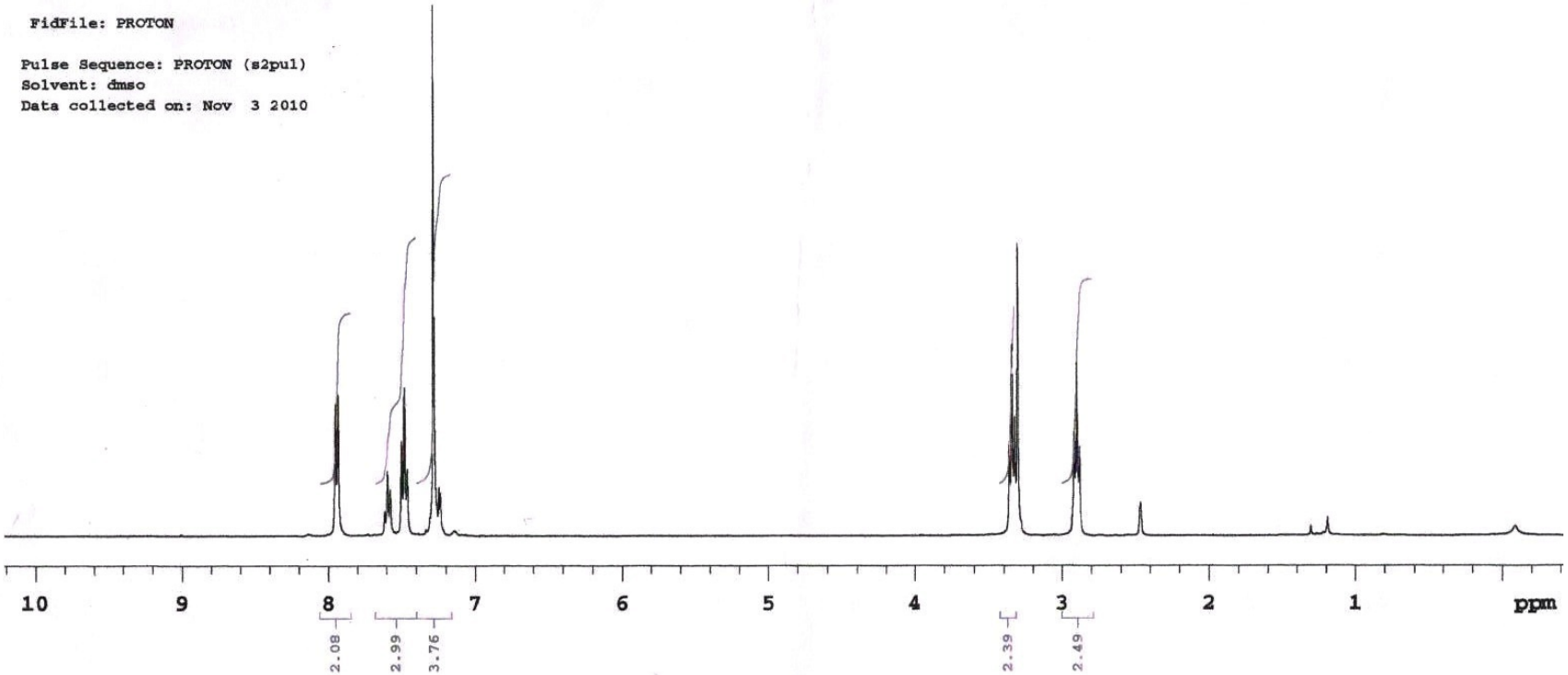


Table 3 entry 8, ^{13}C

3-(4-chlorophenyl)-1-phenylpropan-1-one

R.No-042

exp1 s2pul

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ACQUISITION		**FLAGS**	
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fb	13200	hs	nn
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tpwr	56	rp	-124.7
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DECOUPLER		**PLOT**	
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dof	0	sc	0
dm	yyy	vs	135
dmm	w	th	4
dpwr	39	nm	ph
dmf	11300		

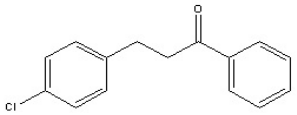


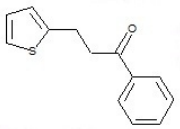
Table 3 entry 10, ^{1}H

1-Phenyl-3-thiophen-2-yl-propan-1-one

045-Crude
1H DMSO-d6
File Ref No :09-111110
MR 400

Analyst : SACHIN

File : xp
Sample id : tmpstudy
Sample : 045-Crude



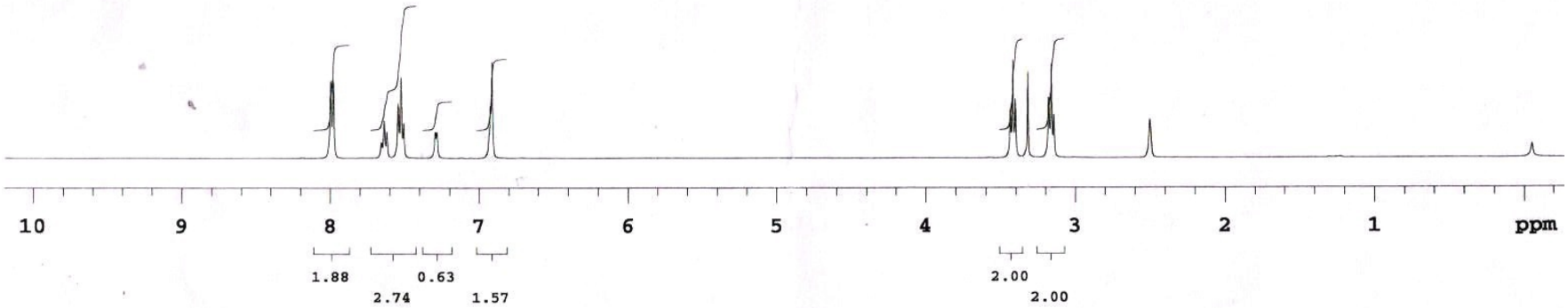


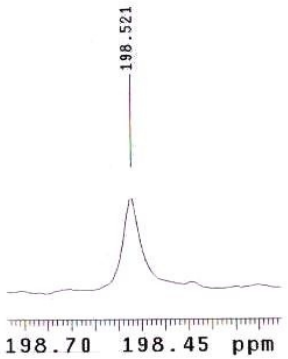
Table 3 entry 10, ^{13}C

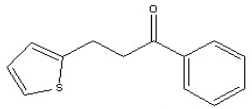
1-phenyl-3-(thiophen-2-yl)propan-1-one

R.No-045

exp3 s2pul

SAMPLE		SPECIAL	
date	Mar 4 2011	temp	not used
solvent	DMSO	gain	2
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	23980.8	pw90	11.500
at	1.815	alfa	20.000
np	87052	FLAGS	
fb	13200	il	n
bs	4	in	n
d1	3.000	dp	y
nt	12000	hs	nn
ct	100	PROCESSING	
TRANSMITTER		lb	2.00
tn	C13	fn	not used
sfrq	75.430	DISPLAY	
tof	748.9	sp	-60.5
tpwr	56	wp	16637.9
pw	4.750	rfl	6727.0
DECOUPLER		rfp	2979.2
dn	H1	rp	-127.4
dof	0	lp	-334.1
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	39	sc	0
dmf	11300	vs	49
		th	4
		nm	ph





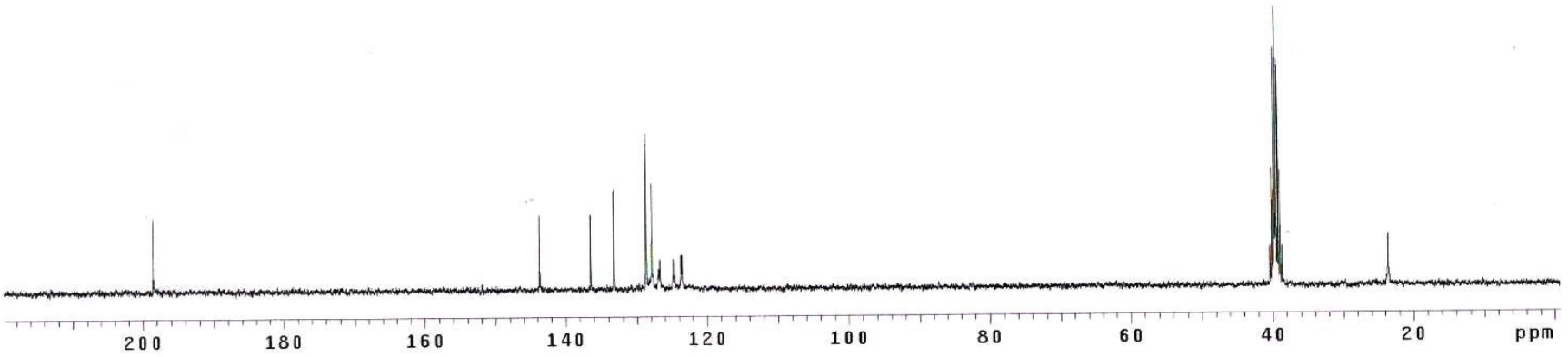


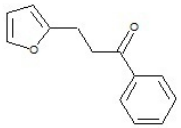
Table 3 entry 11, ^{1}H

3-Furan-2-yl-1-phenyl-propan-1-one

066-Crude
1H DMSO-d6
File Ref No :09-111110-28
MR 400

Analyst : SACHIN

File : xp
Sample id : tmpstudy
Sample : 066-Crude



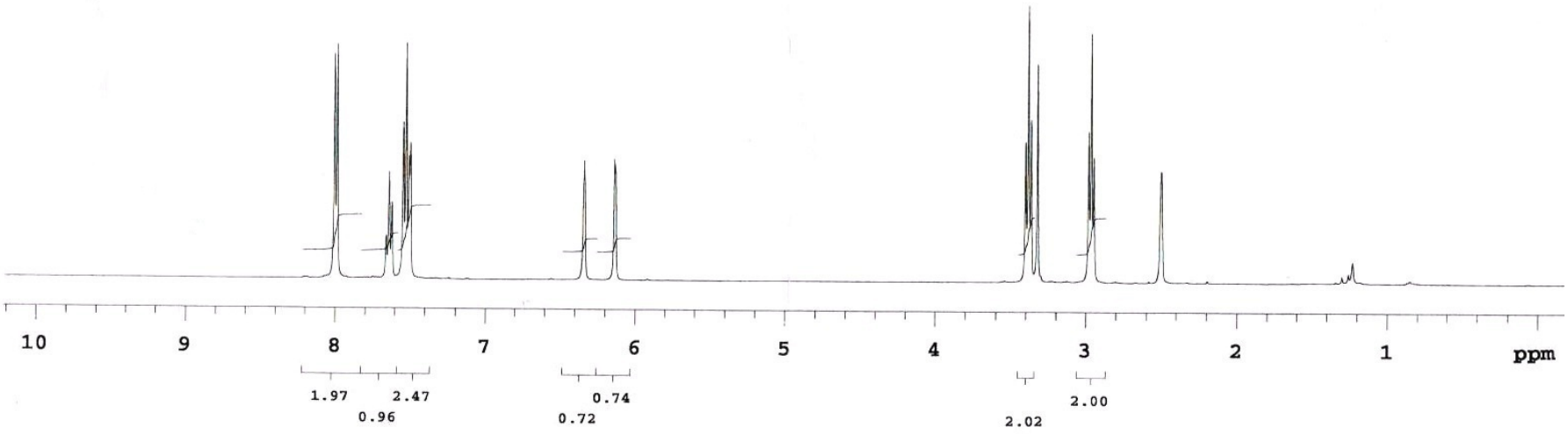


Table 3 entry 11, ^{13}C

3-(furan-2-yl)-1-phenylpropan-1-one

R.No-066

exp3 s2pul

SAMPLE		SPECIAL	
date	Mar 4 2011	temp	not used
solvent	DMSO	gain	2
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	23980.8	pw90	11.500
at	1.815	alfa	20.000
np	87052	FLAGS	
fb	13200	il	n
bs	4	in	n
d1	3.000	dp	y
nt	12000	hs	nn
ct	1156	PROCESSING	
TRANSMITTER		lb	4.00
tn	C13	fn	not used
sfrq	75.430	DISPLAY	
tof	748.9	sp	-27.9
tpwr	56	wp	16575.0
pw	4.750	rfl	6726.3
DECOUPLER		rfp	2979.2
dn	H1	rp	-136.3
dof	0	lp	-307.2
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	39	sc	0
dmf	11300	vs	414
		th	4
		nm	ph